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Modification by Surfactants of Soil Water Absorption

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This work describes the application of a previous study which dealt primarily with organic synthesis and physical properties of reaction products of pure fatty acids with DETA. Derivatives to amplify the previous study were prepared from various industrial fatty materials. The reaction product, from 1 mole diethylenetriamine (DETA) with 2 moles fatty acid, was thought to be the primary amine, $RCON(CH_2CH_2NH_2)$-CH_2CH_2NHCOR, rather than the secondary amine, as cited in the literature. The amine was readily dehydrated to the imidazoline, $RC = NCH_2CH_2NCH_2CH_2NHCOR$. The imidazolines in the presence of moisture hydrolyzed upon standing, to the open chain derivatives. These cationic surfactants were examined as water repellents for soil. Water repellency was evaluated by contact angle measurements and water infiltration through sand, sandy soil, and soil containing 30% clay. A large number of derivatives made clay soil hydrophobic, whereas only a few caused this effect on sandy soils. The following factors influenced soil water repellency. Open chain derivatives were more hydrophobic than the corresponding imidazolines. Hydrophobicity intensified with increasing molecular weight of the saturated fatty acids. Unsaturation, as in the oleic acid derivatives, enhances hydrophilicity. Hydrocarbon branching in the fatty acid also reduces water repellency. The soil hydrophobing agents in treated soils greatly restrict seed germination.

Farming, particularly in arid areas, requires efficient utilization of water. Over the years several methods have been developed to harvest water. Water harvesting is the process of collecting water from plots that have been made water repellent so that the runoff from these plots may be employed in agriculture. Physical waterproofing methods, such as coating the ground with nylon sheets, asphalt, fuel oil, and paraffin wax (1) have appeared in the literature; however, references to chemical interactions with the soil to produce hydrophobic surfaces are few (2, 3). A chemical soil treatment would provide an alternative means of harvesting water.

A search of the chemical literature suggested that surfactants, containing amine groups, might impart water repellent properties to soils. While studying the cation exchange mechanism of large substituted ammonium ions on clay, Gieseking (4) found that clays saturated with the organic ammonium ions did not show the water absorption, swelling, and dispersion characteristics of untreated clay. Subsequently, Law and Kunze (5) examined the effects of three different types of surfactants on clays. They reported that commercial cationic surfactants were strongly adsorbed on clay through ionic bonding, in amounts equal to or even greater than the cation-exchange capacities of the clays. According to these authors, the presence of surfactants on clays significantly reduced hydration and water content at high treatment rates. Furthermore, Greenland (6) observed that cationic surfactants created a layer of increased hydrophobic character beneath the soil's surface.

Various types of cationic surfactants were reviewed by us to select one, relatively low in cost and readily prepared on a large scale, for which the relationship of chemical structure to surface active properties could be conveniently studied.

One type of cationic surfactant was the fatty acid derivatives of polyamines. The properties of the derivatives of fatty acids and ethylenediamine have been described in the literature (7-9). It appeared from these reports that the 2-alkyl-2-imidazolines would not impart sufficient hydrophobicity to soils. However, the analogous series of homologous compounds from the fatty acids and diethylenetriamine (DETA) appeared likely to do so because of their higher molecular weight.

In 1940, Ackley (10) reacted fatty acids with DETA to form precursors for fabric softeners. However, it was not until recently (11) that the course of the reaction between fatty acids and DETA, and properties of the reaction products were studied. The reaction appears to proceed, according to the following scheme:

$$RCO_2H + HN(CH_2CH_2NH_2)_2 \xrightarrow{90^\circ C} \text{Amine Soap} \xrightarrow{130^\circ C} RCO_2H + RCON(CH_2CH_2NH_2)_2$$

$$\xrightarrow[6\ \text{hr}]{150^\circ C} RCON(CH_2CH_2NH_2)CH_2CH_2NHCOR$$

$$\xrightarrow[\text{Vacuum}]{150^\circ C,\ 2\ \text{hr}} R\text{-}C{=}N\text{-}CH_2CH_2\text{-}N\text{-}CH_2CH_2NHCOR + H_2O$$

Initially, one molecule of fatty acid reacted with the secondary amine of DETA, followed by a second fatty acid molecule, reacting with one of the two primary amines. The product formed was the N-(2-aminoethyl) diamide, which will be referred to as the diamide. The diamides could be cyclized by heating under vacuum to form imidazolines, which were unstable to hydrolysis. In the presence of water, or upon exposure to atmospheric moisture, they revert back to the diamide.

DETA derivatives of C_9-C_{22} saturated fatty acids, as well as the C_{18} unsaturated acids, oleic and elaidic, were prepared and evaluated in the previous publication (11). Hydrophobicity determination, via contact angle measurements, proved to be nondiscriminatory and, therefore, a more meaningful test, the sand penetration test was devised. The results of this test demonstrated that the diamides of the C_{14} and higher saturated fatty acids were water repellents. On the other hand, the unsaturated oleic acid derivatives enhanced hydrophilicity.

Materials and Methods

Apparatus. Infrared spectroscopy, Perkin-Elmer Model 257 infrared spectrophometer, Perkin-Elmer Corporation (Norwalk, CT); ultraviolet spectroscopy, Perkin-Elmer Model 559 UV-vis spectrophotometer, Perkin-Elmer Corporation, Coleman

Instruments Div. (Oak Brook, IL); Fisher-Johns melting point apparatus, Fisher Scientific Company (Pittsburgh, PA); contact angles, Gaertner goniometer, Gaertner Scientific Corporation (Chicago, IL).

Reagents. The following chemicals were used: diethylenetriamine, Aldrich Chemical Company (Milwaukee, WI); C_{12}, C_{14}, C_{16}, C_{18} saturated fatty acids, Armak Industrial Chemicals Division (Chicago, IL); oleic acid, A. Gross & Company (Newark, NJ); elaidic acid, laboratory preparation (12); tallow, Corenco Corporation (Philadelphia, PA) (titer, t = 42°, iodine no. 40); tallow fatty acid (T - 22) and partially hydrogenated tallow fatty acid (T - 11), Proctor & Gamble, Industrial Chemicals Division (Cincinnati, OH) (T - 22, t = 40°, I. no. = 60) (T - 11, t = 46°, I. no. = 41); hydrogenated tallow fatty acids, Acme-Hardesty Company, Incorporated (Jenkintown, PA), (t = 62°, I. no. = ——); tall oil fatty acids, Arizona Chemical Company (Wayne, NJ) (t = 24°, I. no. = 75); MO-5 fatty acid, Union Camp Corporation (Jacksonville, FL) (t = 33°, I. no. 75); isostearic acid, Emery Industries Incorporated (Cincinnati, OH) (t = liquid, I. no. = 12).

Drierite, W. A. Hammond Drierite Company (Xenia, OH); Ottawa Sand ASTM, Arthur H. Thomas Company (Philadelphia, PA); SYLON-CT Silylating Reagent, Supelco, Incorporated (Bellefonte, PA).

Soils. Granite Reef soil is a sandy loam soil, supplied by the U.S. Water Conservation Laboratory, USDA, Phoenix, AZ. Walla Walla soil is a soil which contains 30% clay and organic matter, supplied by the Columbia Plateau Conservation Research Center, USDA, Pendleton, OR.

Experimental

Preparation of commercial fatty acid-DETA derivatives: the previously described procedure (11) was slightly modified, using a 5% excess fatty acid to ascertain that all DETA was consumed. Amine analysis was conducted, according to AOCS test method (13). The reaction products were used without purification.

Procedures for infrared and ultraviolet absorption and contact angle measurements are reported in the previous publication (11).

Infiltration Tests

Sand Penetration Test

Ten grams of indicating Drierite was placed in a 120-mL silylated jar and covered with 80 g treated ASTM Ottawa sand, prepared according to the previous report (11). The depth of the soil was 35 mm. Distilled water, 8 mL, was then placed on the surface of the sand. The time required to change the indicating Drierite completely from blue to pink was recorded as the infiltration time.

Soil Infiltration Test

A soil infiltration test was devised to screen a large number of compounds within a limited time span. The amounts used are far in excess of quantities used in field application. A 5% diamide solution in isopropanol, 15 mL, was added to 50 g soil, air dried overnight, and then placed in a vacuum oven at 50° for 1 hr to remove traces of isopropanol. The treated soil, 10 g, was placed in a 25 X 500 mm glass chromatographic column with a coarse porosity fritted disc on top of a detachable adapter base. The soil was tapped down lightly with a wooden dowel to a depth of 12 mm in order to prevent channeling. Forty-five cm of water covered the soil. The period required for 200 mL distilled water to penetrate through 10 g of treated soil was recorded as the infiltration time. The test was arbitrarily discontinued after 2 weeks.

Glycerine Effect on Hydrophobicity. The partially hydrogenated tallow fatty acid-DETA reaction product, 10 g, was weighed into each of five 60-mL bottles. The following amounts of glycerine, expressed as percent, were weighed, using an analytical balance, into the bottles: 0.36, 1.02, 2.60, 5.10, 11.11. Mixtures were then melted and stirred. Contact angles were measured, according to the procedure in the previous publication (11).

Soil Extraction. Granite Reef soil, 100 g, was treated with 30 mL of a 5% isopropanol solution of the partially hydrogenated tallow fatty acid-DETA reaction product and then air dried overnight and finally in a vacuum oven at 50°C for 1 hr to remove residual isopropanol. On the following day the treated soil was extracted with ethanol 8 hr in the Soxhlet apparatus. The extracted solvent was evaporated recovering 1 g residue. As a control experiment, untreated soil, 100 g, was also extracted 8 hr with ethanol, recovering 0.2 g material. The dried extracted soil was placed in the chromatographic column and the infiltration test with 200 mL distilled water repeated.

Plant Growth Effect Test. Potting soil, 3.4 kg, was weighed into a 55 X 27.5 X 7.5 cm flat, treated with 1.2 L of a 5% solution of the partially hydrogenated tallow fatty acid-DETA diamide in isopropanol, and air dried for 2 days until the isopropanol had evaporated. Untreated potting soil, 3.4 kg, was weighed into another flat to be used as a control.

Soybeans

Fifty soybean seeds each were planted in the diamide-treated soil as well as in a flat with an untreated control soil. Each flat was watered weekly with 2 L tap water. Water absorption and plant growth were recorded.

Corn

Since the nitrogen requirement of corn plants is greater than the nitrogen content found in potting soil, additional nitrogen fertilizer, 15 g 20:20:20/2 L water, was added to the soil, prior to treatment with water repellent chemicals. Fifty corn kernels were planted in the treated soil and an untreated control flat. The flats were watered weekly as described above, and growth recorded. After several weeks the plants were harvested, weighed, and dried in a vacuum oven and weighed again.

Results and Discussion

This work describes the application to soil of compounds of a previous study (11) which dealt primarily with organic synthesis and physical properties of reaction products of pure fatty acids with DETA. In this study derivatives were prepared from various industrial fatty materials. In addition, water infiltration studies on sand, sandy soil, and clay soils were carried out on the previously prepared and new compounds. Finally, an investigation was initiated to determine the biological effects of one water-repelling chemical, the partially hydrogenated tallow-fatty acid-DETA reaction product, on seed germination and plant growth.

The DETA derivatives from industrial fatty materials for soils application were of special interest because of their ready availability, low cost, and greater solubility than the DETA derivatives from the purified fatty acids. Diamides were prepared from tallow, tallow fatty acids, partially hydrogenated tallow fatty acids, hydrogenated tallow fatty acids, tall oil fatty acids, MO-5 acids (a mixture of oleic, isooleic, stearic, and elaidic acids), and isostearic acid (a mixture of branched chain isomeric acids).

Melting points and contact angle measurements of the fatty acid-DETA reaction products are recorded on Table I. The melting points of the pure saturated fatty acid-DETA derivatives were over 100°C and possessed low solubility in most organic solvents. The unsaturated fatty acid-diamides had much lower melting points. The industrial fatty-DETA derivatives with the exception of the product from hydrogenated tallow fatty acids melted at 60°C or below.

Contact Angle Measurements. It was planned to establish the hydrophilic or hydrophobic nature of the diamides by contact angle determination (14). The angles for the lauric diamides and higher saturated homologs were all above 90°. Thus, the contact angle measurements did not discriminate between members of a homologous series. The unsaturated fatty acid-DETA derivatives were predictably more hydrophilic. Among the industrial fatty acid-DETA derivatives, only three possessed contact angles over 90°. These were the DETA derivatives of partially and fully hydrogenated tallow fatty acids and the isostearic acid. Although a 50:50 mixture of DETA derivatives of isostearic and partially hydrogenated tallow fatty acids produced a compound with the desired melting point, the contact angle of this mixture fell to 73°. The data are reported in Table I.

Sand Penetration Tests. Since contact angle measurements appeared fairly insensitive to structure differences, a sand penetration test was devised. Water penetration rates through beds of treated sand were determined for the derivatives of the individual pure fatty acids, as well as for those from the industrial fatty materials as shown in the first column of Table II. Water passed quickly through the C_{12} diamide-treated sand, whereas a period of 7 or more days was required for the C_{14} and higher molecular weight-saturated diamides. While water penetrated the oleic diamide-coated sand within 5 min, 1-day was required for penetration of the elaidic diamide-coated sand, showing the superiority of the trans isomer. In the cis configuration, the molecule is bent back upon itself, resulting in properties

Table I. Physical Properties of Diethylenetriamine Reaction Products

R-COOH	Melting Point, C	Contact Angle (°)
$C_{11}H_{23}$	110-111	99
$C_{13}H_{27}$	112-113	99
$C_{15}H_{31}$	116-117	96
$C_{17}H_{35}$	118-119	98
Δ^9 $C_{17}H_{33}$, cis	52-53	50
Δ^9 $C_{17}H_{33}$, trans	91-92	62
Derivatives of Industrial Fatty Materials		
Tallow	50-60	37
Tallow Fatty Acid[a]	45-55	63
Tallow Fatty Acid[b]	55-65	97
Hyd. Tallow F.A.	90-95	94
Tall Oil F.A.	35-45	59
MO-5	30-40	56
Isostearic	30-40	91
Isostearic + Tallow Fatty Acid[b] (50:50)	40-45	73

[a] = T-22 fatty acids, C_{18} cis = 36%, C_{18} trans = 7%

[b] = T-11 fatty acids C_{18} cis = 6%, C_{18} trans = 24%

Table II. Infiltration Properties of Diethylenetriamine Reaction Products

DETA-Fatty Acid Derivative from	Sand Penetration	Granite Reef Soil Infiltration	Walla Walla Soil Infiltration
$C_{11}H_{23}COOH$	1 hr	3 hr	5 hr
$C_{13}H_{27}COOH$	7 d	5 d	>2 wk
$C_{15}H_{31}COOH$	>7 d	5 d	>2 wk
$C_{17}H_{35}COOH$	>7 d	>2 wk	>2 wk
Δ^{9} $C_{17}H_{33}$ cis COOH	5 min	3 hr	8 hr
Δ^{9} $C_{17}H_{33}$ trans COOH	1 d	>2 wk	2 wk
Tallow	i[c]	4 hr	8 hr
Tallow Fatty Acid[a]	i	1 d	>2 wk
Tallow Fatty Acid[b]	i	1 wk	>2 wk
Hyd. Tallow F.A.	>7 d	>2 wk	>2 wk
Tall Oil F.A.	i	4 hr	8 hr
MO-5	i	2 hr	8 hr
Isostearic	i	2 hr	7 hr
Isostearic + Tallow F.A.[b] (50:50)	i	3 hr	2 wk
Control	i	4 hr	1 d

[a] = T-22 fatty acids

[b] = T-11 fatty acids

i[c] = instantaneous

roughly analogous to those of a C_9 fatty acid derivative. Although the elaidic diamide derivative is more linear in configuration than the oleic diamide, the trans unsaturation disarranges the molecules, resulting in surface properties which are less hydrophobic compared to those of the saturated stearic acid derivative. These observations help explain the results obtained with the industrial fatty acid derivatives. Instantaneous penetration was observed for sand treated with the DETA derivatives of tallow, tallow fatty acids, tall oil fatty acids, and MO-5 acids as predicted by their low contact angles. All of these are high in oleic acid content. In contrast, sand treated with the completely hydrogenated tallow fatty acid-DETA diamide which had a high contact angle required more than 1 week for water penetration. In these two sets of examples, correlation as to degree of hydrophobicity was observed between the sand penetration tests and the contact angle measurement.

However, with the other derivatives there was disagreement. Water immediately penetrated sand coated with the DETA derivatives of partially hydrogenated tallow fatty acids and isostearic acid, despite their high contact angles of greater than 90°. Water quickly passed through sand treated with a 50:50 mixture of diamides of isostearic acid and partially hydrogenated tallow fatty acids. While these penetration results on standardized ASTM sand were interesting, they did not forcast the results found with sandy and clay soils.

Soil Column Tests. In the sand penetration test, a minimal amount of water was used. No consideration was given to the hydrostatic pressure which would occur in nature from a body of surface water. A new soil infiltration test was developed to take this into consideration. This test used a maximum amount of water (200 mL) on a minimum amount of treated soil (10 g) and was restricted only by the dimensions of the laboratory equipment. Our aim was to prepare an hydrophobe for soil which would support water over an extended period of time. Whereas water passed through soil treated with hydrophilic compounds within 8 hr, 2 weeks or more were required for penetration through an hydrophobe-treated soil. In the latter case the water level dropped 6 mm or less each day, showing that the cationic surfactant greatly hindered, but did not completely restrict the passage of water. The tests were usually terminated after 2 weeks, due to the large number of samples to be tested. The two soils were selected because of differences in composition and properties. The results of the soil infiltration test are recorded in Table II.

Although the infiltration times differed slightly from each other, due to differences in soil structure, water passed quickly through soil treated with hydrophilic compounds, whereas a week or longer was required for passage through hydrophobic-treated soil. Water penetrated soil treated with the lauric acid diamide more rapidly than the controls, demonstrating the hydrophilic nature of the C_{12} derivative. A much longer time period was required for penetration through soils, treated with the saturated C_{14} and above diamides. Drastic differences were observed for the infiltration times of soils treated with the cis unsaturated oleic acid diamide (hr) compared to the trans unsaturated elaidic acid diamide (wk).

The industrial fatty acid-DETA derivatives were evaluated for application to soil. Water infiltrated soil coated with the DETA derivative of tallow more rapidly than the controls. This was due to the high unsaturation content and also in part to the glycerine retained in the product as discussed below. We were unable to find a solvent system which would readily separate the glycerine, formed from the triglyceride, from the DETA reaction product. If the glycerine were removed, the infiltration rates for the tallow-DETA derivative should be identical with the rates obtained for tallow fatty acid-DETA reaction product.

The soil treated with the tallow fatty acid-DETA reaction product retarded moisture infiltration on both soils. The partially hydrogenated and completely hydrogenated tallow fatty acid-DETA derivatives also displayed hydrophobic properties on both soils. Although the completely hydrogenated tallow fatty acid-DETA reaction product (m.p. 90°C) had optimum hydrophobic properties on all three soils, it was difficult to dissolve in most organic solvents. Even the partially hydrogenated tallow fatty acid-DETA reaction product, m.p. 45°-50°C, was not readily soluble. To overcome this difficulty, we examined the DETA derivatives of some other fatty materials, hoping to find an hydrophobe with a lower melting point.

Water infiltration tests were conducted on soils treated with the DETA derivatives of tall oil fatty acids, MO-5 acids, and isostearic acid, all of which melted below 45°. Water infiltrated sandy soil treated with these compounds within 4 hr and through clay containing soil within 8 hr, confirming their hydrophilic nature. The blending of these diamides into the tallow derivatives in order to lower melting points and enhance solubility causes a serious loss of hydrophobicity in sandy soil. For example infiltration rates dropped from 1 week to 3 hr passing water through Granite Reef soil treated with a 50:50 mixture of DETA derivatives of isostearic acid and partially hydrogenated tallow fatty acids. The water infiltration rate on Walla Walla soil, treated with the 50:50 mixture, remained similar to that obtained with the partially hydrogenated tallow fatty acid-DETA derivative alone.

The soil properties observed with these chemicals suggest that the chemical structural requirements for an hydrophobic cationic surfactant appear to be:

a. Molecular weight > 500.
b. Prepared from saturated starting materials.
c. Contain free amino groups to attach to soil particles.

Glycerine Effect on Hydrophobicity. The tallow-DETA reaction product, containing over 10% free glycerine, had a contact angle of 37°. Glycerine in measured amounts was added to the partially hydrogenated tallow fatty acid-DETA reaction product and contact angles measured (See Figure 1). The purpose was to determine how much glycerine a reaction product could tolerate and yet remain hydrophobic. The results show that glycerine amounts of as low as 1% render the reaction product hydrophilic and suggest that tallow fatty acids rather than tallow be used in the synthesis of DETA reaction products.

Retention on Soil. An experiment was conducted to demonstrate the retention of the cationic surfactant on the soil. Granite Reef soil, treated with the partially hydrogenated tallow fatty acid-DETA reaction product together with an untreated soil sample was extracted in the Soxhlet apparatus. The extracted soils were returned to the chromatographic column and the water infiltration test repeated. It has been reported previously (15) that short-chain alcohols form double layer complexes on the surface of soil particles, causing a modification of soil properties. Whereas water penetrated the untreated, unextracted Granite Reef soil control in 4 hr, 12 hr was now required for passage through the untreated, alcohol extracted soil. Water penetration through extracted treated soil was incomplete after 4 days, showing that the water repelling agent remained on the soil. Fripiat and coworkers (16) have reported that amines can protonate in soil and replace inorganic cations from the clay complex by ion exchange. Amines are adsorbed with their hydrocarbon chains perpendicular or parallel to the clay surface, depending on the concentration (16). The surface of the soil particles has now become hydrophobic and delays the passage of water molecules.

The material (1 g) recovered by the alcoholic extraction of treated soil in the Soxhlet apparatus was identified by U.V. spectroscopy at 202 nm as being unreacted partially hydrogenated tallow fatty acid-DETA reaction product. The alcohol solubles from the untreated soil absorbed in the range of 230-220 nm with only a trace absorption at 202 nm. The 60% recovery suggests that the 5% concentration was too high and further work is required to determine the proper concentration.

Effects on Plant Growth. Experiments were initiated to determine the effect of a soil hydrophobe on seed germination. Potting soil was treated with the partially hydrogenated tallow fatty acid-DETA reaction product. Although no crust formed on the soil's surface after the addition, a coarser texture of the potting soil was observed. In reviewing plants which would germinate rapidly, soybeans were selected. After the seeds were planted in the treated soil, as well as an untreated control, the flats were watered weekly. We were surprised to see water roll off and down the sides of the treated flat. Whereas the control flat took up 1.7 kg of water, the treated soil flat gained only 110 g. The soybeans in the control flat germinated in 10 days and grew rapidly. After a period of 8 weeks, one seed germinated in the hydrophobe-treated soil (See Figure 2). This experiment was continued for another month, but no further plants appeared. The seeds were not able to germinate because the passage of water through the soil was blocked.

Corn was used to demonstrate the effects of soil hydrophobes on the cereal grasses. After adding nitrogen fertilizer, the potting soil was treated with the partially hydrogenated tallow fatty acid-DETA reaction product. As a result of this enrichment all seeds germinated in the treated soil and in the control. However, the corn plants grown in the treated soil soon developed a yellow cast and appeared stunted in growth. After 6 weeks the corn plants were harvested. The stalks planted in the treated soil weighed 54% of those grown in the control. The stalks were then dried in a vacuum oven to constant weight, and the plants from the hydrophobe-treated soil now weighed 47% of the control plants. These results show that the growth of plants was greatly impeded by the surfactant.

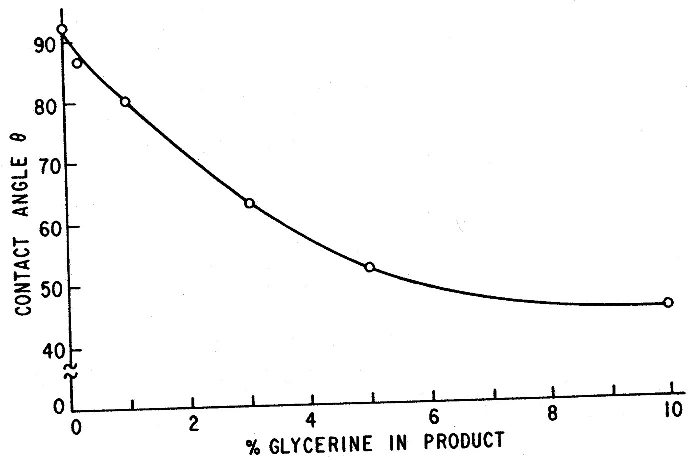

Figure 1. Effect of glycerine concentration on contact angle the partially hydrogenated tallow fatty acid-DETA reaction product.

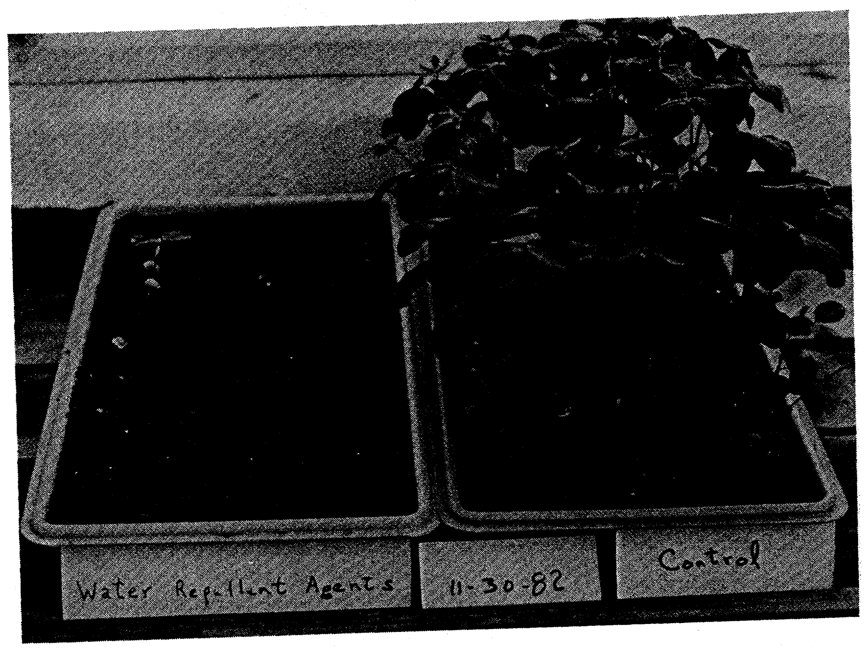

Figure 2. Effect of soil hydrophobe on soybean germination.

Acknowledgments

D. Brower and M. P. Thompson carried out the plant experiments.

Literature Cited

1. Fink, D. H.; Cooley, K. R.; Frasier, G. W. J. Range Manage. 1973, 26, 396.
2. Myers, L. E.; Frasier, G. W. J. Irrig. Drain. Div. Amer. Soc. Civil Engin. Pro. 1969, 95, 43.
3. Fink, D. H.; Frasier, G. W. Soil Sci. Soc. Am. Publication #7,1975,173. ASCE 1969, 95, 43.
4. Gieseking, J. E. Soil Sci. 1939, 47, 14.
5. Law, J. P., Jr.; Kunze, G. W. Soil Sci. Soc. Am. Proc. 1966, 30, 321.
6. Greenland, D. J. Soc. Chem. Ind. Monograph 1970, 37.
7. Shapiro, S. H in "Fatty Acids and Their Industrial Application"; Pattison, E. S., Ed.; Marcel Dekker, Inc.: New York, NY, 1968; p. 98.
8. Ferm, R. J.; Riebsomer, J. L. Chem. Rev. 1954, 54, 593.
9. Tornquist, J. Proc. of the 4th International Congress on Surface Active Substances, Vol. 1, Sect. A, Gordon and Breach Science Publishers, London, England, 1967, p. 387.
10. Ackley, R. R.; U.S. Patent 2,200,815, 1940.
11. Bistline, R. G., Jr.; Hampson, J. W.; Linfield, W. M. J. Am. Oil Chem. Soc. 1983, 60, 823.
12. Swern, D.; Scanlan, J. T. Biochem. Prep. 1953, 3, 118.
13. AOCS Test Method TF 1b-64 and TF 2b-64 "Quantitative Determination of Amines"; Am. Oil Chem. Soc.: Champaign, IL, 1979.
14. Rosen, M. J. in "Surfactants and Interfacial Phenomena"; John Wiley & Sons; New York, NY, 1978; p. 179.
15. German, W. L.; Harding, D. A. Clay Miner. 1971, 9, 167.
16. Fripiat, J. S.; Servias, A.; Leonard, A. Bull. Soc.: Chim., France 1962; p. 635.

RECEIVED January 10, 1984

Reprinted from ACS Symposium Series, No. 253
Structure/Performance Relationships in Surfactants
Milton J. Rosen, Editor